PB90-146291

Determination of Rates of Reaction in the Gas-Phase in the Troposphere: Theory and Practice. 2. Rate of Direct Photoreaction

(U.S.) Environmental Protection Agency, Washington, DC

Nov 89

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA 560/5-89-007 PB90-146291

DETERMINATION OF RATES OF REACTION IN THE GAS-PHASE IN THE TROPOSPHERE

THEORY AND PRACTICE

2. Rate of Direct Photoreaction: Screening-Level Test Guideline § 796.3800. Laboratory Spectroscopic Determination of the Cross Section and the Maximum Rate of Direct Photoreaction in Sunlight

by

Asa Leifer

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, DC 20460

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50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. EPA 560/5-89-007	2.	3. Recipient's Accession No.
4. Title and Subtitle Determination of Rates of Reaction in the Gas-Phase in the Troposphere. Theory and Practice. 2. Rate of Direct Photoreaction: Screening-Level Test Guideline-Spectroscopic Determination of the Cross Section and the Maximum Rate of Direct Photoreaction in Sunlight			5. Report Date November 1989 6.
7. Author(s) Asa Leifer			8. Performing Organization Rept. No.
9. Performing Organization Name and Address U.S. Environmental Protection Agency Office of Toxic Substances Exposure Assessment Branch (TS-798) 401 M Street, SW Washington, DC 20460			10. Project/Task/Work Unit No. 11. Contract(C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address U.S. Environmental Protection Agency Office of Toxic Substances 401 M Street SW Washington, DC 20460			13. Type of Report & Period Covered 14.
15. Supplementary Notes			

16. Abstract (Limit: 200 words)

This report describes in detail a simple and cost-effective screening test for estimating an environmentally relevant maximum rate constant and minimum half-life for direct photoreaction of a chemical in the gas-phase in the troposphere. This report has two main sections: PART I. THEORY AND DEVELOPMENT OF THE SCREENING TEST AND PART II. TEST PROCEDURES AND DATA REPORTING. PART II describes detailed procedures for measuring the cross section of a chemical in the gas-phase in the laboratory by spectroscopic techniques and data reporting for sections 4 and 5 of TSCA. Tables of solar irradiance (J_λ) are given from 0° to 70° North latitude in 10° increments as a function of season of the year to cover the continental United States and other parts of the U.S. such as Alaska, Hawaii, etc. An example is given to illustrate how to use all the experimental cross section data and solar irradiance data (J_λ) to estimate the maximum rate of direct photoreaction $[k_{dE}]_{max}$ and the minimum half-life $[t_{(1/2)E}]_{min}$.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

Rate of direct photoreaction in the troposphere, Screening-level test method, maximum direct photoreaction rate constant, minimum half-life for direct-photoreaction, absorption spectroscopy in the gas-phase, cross section, test guideline for the Toxic Substance Control Act, Sunlight photoreaction, Tables of solar irradiance

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Release Unlimited	Unclassified	48
	20. Security Class (This Page)	22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

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Abstract

This report describes a simple and cost-effective screening test for estimating an environmentally relevant maximum rate constant for direct photoreaction of a chemical in the gas-phase in sunlight and the corresponding minimum half-life.

Based on the theory of direct photoreaction of a gaseous chemical in sunlight in the troposphere, it has been shown that $[k_{dE}]_{max} = 2.303 \sum_{\lambda} \sigma'_{\lambda} J_{\lambda}$ where σ'_{λ} is the cross section of a gaseous chemical in the decadic logarithm system and J_{λ} is the actinic flux, or solar irradiance, in the troposphere. Using the Beer-Lambert law and spectroscopic techniques, a detailed experimental procedure is described for determining σ'_{λ}, the decadic cross section of a chemical in the gas-phase. Tables of J_{λ} are given for the latitudes 0 to 70° N. in 10° increments as a function of season of the year to cover the continental United States and other parts of the U.S. such as Alaska, Hawaii, etc. The maximum direct photoreaction rate constant $[k_{dE}]_{max}$ is obtained by calculating the products $\sigma'_{\lambda} J_{\lambda}$ and summing these results over λ where the chemical absorbs light (i.e., where σ'_{λ} is nonzero). The minimum half-life is given by $[t_{(1/2)E}]_{min} = 0.693/[k_{dE}]_{max} = 0.301 \Big/ \sum_{\lambda} \sigma_{\lambda} J_{\lambda}$.

An example is given to illustrate how all the experimental cross section data is used to estimate $[k_{dE}]_{max}$ and $[t_{(1/2)E}]_{min}$.

PART I. THEORY AND DEVELOPMENT OF THE SCREENING TEST

I.A. Introduction

Numerous chemicals, both natural and anthropogenic, are emitted into the troposphere from a variety of sources and may be removed by wet or dry deposition or they may be transformed by several reaction pathways. These reaction pathways are: (1) direct photoreaction which involves the absorption of sunlight, followed by transformation; (2) indirect photoreaction which involves the reaction of a chemical with hydroxyl radicals (OH); and (3) oxidation, which involves the reaction of a chemical with ozone (O_3). A quantitative measure of these three processes is given by the rate constants k_{dE}, k_{OH}, and k_{O_3}. The rate constant k_{dE} represents the first-order rate constant for direct photoreaction while k_{OH} and k_{O_3} represent second-order rate constants for indirect photoreaction with OH radicals and oxidation with O_3, respectively.

A two-tiered hierarchal test scheme has been developed for determining the rate constants k_{dE}, k_{OH}, and k_{O_3} and half-lives $[t_{(1/2)E}]$ in the gas-phase in the troposphere Leifer [USEPA (1989)]. This report describes a cost-effective screening test to estimate the maximum direct photoreaction rate constant $[k_{dE}]_{max}$ and the minimum half-life $[t_{(1/2)E}]_{min}$ in the troposphere.

I.B. Development of the Screening Test: Laboratory Determination of the Gas-Phase Cross Section and the Maximum Rate of Direct Photoreaction

I.B.1. Theoretical Aspects

Radiation from the sun is the driving force for tropospheric photochemistry. In a polluted urban troposphere, chemical species are produced and destroyed by a complex process that involves numerous specific kinetic reactions. The primary pollutants NO_x (i.e., NO, NO_2, etc.) react with organic chemicals and sunlight to form a number of intermediates (e.g., the hydroxy radical and the hydroperoxy radical). These intermediates generate a host of secondary pollutants such as ozone, formaldehyde, nitric acid, nitrous acid, etc. (Finlayson-Pitts and Pitts (1986)]. These pollutants absorb sunlight and enter into a wide range of photochemical processes. Clearly, the absorption of sunlight by chemicals in the troposphere and the resultant chemical products are strongly dependent on the incident solar radiation in the troposphere.

The troposphere receives ultraviolet and visible radiation during the day directly from the sun, by scattered light from the sky, and by reflection from the earth's surface. The quantity of radiation received in the troposphere is dependent on the solar irradiance outside the earth's atmosphere, the solar zenith angle, scattering, diffusion, absorption by the earth's atmosphere, and the reflection of sunlight from the surface of the earth. Furthermore, the amount of radiation absorbed by

chemical species within the polluted layer in the troposphere depends on the radiation received, the absorption coefficient and the concentration of the chemical species, and on the path length. Leighton carried out extensive research in the 1950's on the photochemical processes that occur in the atmosphere, many of his computational results were first reported in 1956 [Leighton and Perkins (1956)], and much of this work was published in a book in 1961 [Leighton (1961)]. His work describes in detail a simple, yet effective, radiative transfer model to calculate the actinic flux (i.e., solar irradiance) at the earth's surface.

Leighton (1961) has shown that for weak absorbance of a chemical in the atmosphere, the average rate of absorption of sunlight per unit volume by a chemical is

$$I_{a\lambda} = 2.303\,\alpha_\lambda\, j^{-1} C\, [I_{d\lambda}\,\text{secant}(z) + i I_{s\lambda}] \qquad (1)$$

where $I_{a\lambda}$ is the average rate of absorption of sunlight in photons $cm^{-3}\ s^{-1}$, $I_{d\lambda}$ and $I_{s\lambda}$ are the direct and sky solar irradiance in photons $cm^{-2}\ s^{-1}$, z is the solar zenith angle, C is the concentration of chemical, α_λ is the decadic absorption coefficient of the chemical, j is a constant which converts the intensity units into units that are compatible with α_λ and C, and i is a constant (i.e., $\bar{L}_s = ih$, where $\bar{L}_s$ is the average path length of sky radiation traversing a surface layer of the atmosphere of height h). Leighton indicated that to a good approximation i = 2. Leighton called the term in the brackets of

equation 1 J_λ, the actinic flux or irradiance (i.e., solar irradiance), and equation 1 becomes

$$I_{a\,\lambda} = 2.303\,\alpha_\lambda\, j^{-1} C\, J_\lambda \qquad (2)$$

where

$$J_\lambda = [I_{d\,\lambda}\,\text{secant}(z) + iI_{s\,\lambda}] \qquad (3)$$

Letting $\sigma'_\lambda = \alpha_\lambda\, j^{-1}$, equation 2 becomes

$$I_{a\,\lambda} = 2.303\,\sigma'_\lambda\, C\, J_\lambda \qquad (4)$$

where σ'_λ is the cross section of a chemical in cm^2 $molecule^{-1}$, C is the concentration of chemical in molecules cm^{-3}, and J_λ is in photons cm^{-2} s^{-1}.

Using the first and second laws of photochemistry (i.e, the Grotthus-Draper and the Stark-Einstein laws, respectively), the average rate of disappearance of a chemical undergoing direct photoreaction (d) in the gas-phase in the troposphere at a fixed wavelength is given by the expression

$$\text{Average rate} = -(dC/dt)_{d\,\lambda} = I^{d}_{a\,\lambda}\phi_\lambda \qquad (5)$$

where $I^{d}_{a\,\lambda}$ is the average rate of light absorption of sunlight by the chemical at wavelength λ in photons per unit volume (cm^3) per unit time t (s) [the Grotthus-Draper law]; ϕ_λ is the reaction quantum yield of the chemical at λ, the efficiency with which the absorbed light transforms the chemical [the Stark-

Einstein law]; and C is the concentration of the chemical in the units molecules cm^{-3}.

Substituting equation 4 in 5 yields

$$\text{Average rate} = -(dC/dt)_{d\lambda} = 2.303C\,\phi_\lambda \sigma_\lambda J_\lambda \tag{6}$$

and summing equation 6 over all wavelengths of sunlight absorbed by the chemical yields

$$\text{Average rate} = -\sum_\lambda (dC/dt)_{d\lambda} = 2.303C \sum_\lambda \phi_\lambda \sigma'_\lambda J_\lambda \tag{7}$$

By defining the relationships

$$\text{Average rate} = -\sum_\lambda (dC/dt)_{d\lambda} = (dC/dt)_{dE} \tag{8}$$

and

$$k_{dE} = 2.303 \sum_\lambda \phi_\lambda \sigma'_\lambda J_\lambda \tag{9}$$

equation 7 becomes

$$-(dC/dt)_{dE} = k_{dE}\, C \tag{10}$$

where k_{dE} is the first-order direct photoreaction rate constant of a chemical in the troposphere in the environment (E).

Integrating equation 10 under the boundary conditions [$C = C_0$ at $t = 0$] an [$C = C_t$ at t] yields

$$\ln(C_0/C_t) = k_{dE}\, t \tag{11}$$

The half-life $t_{(1/2)E}$ in the environment is defined as the time required for the chemical to reach one-half its initial concentration. Therefore, under this boundary condition $C_t = C_0/2$ and $t = t_{(1/2)E}$; and equation 11 yields

$$t_{(1/2)E} = \ln 2/k_{dE} = 0.693/k_{dE} \qquad (12)$$

Leighton's model and solar irradiance (J_λ) have been a cornerstone in the development of atmospheric chemistry [Leighton and Perkins (1956), Leighton (1961)]. His solar irradiance data have been used to determine photodissociation rate constants of several species, especially NO_2, as a function of time of day or zenith angle. These rate constants have been used in mathematical diffusion modeling of photochemical pollution (Reynolds (1973)] and in the computer simulation of mixtures of reactive chemical species to evaluate various mechanisms for photochemical smog formulation [Demerjian (1974)]. Peterson updated the work of Leighton by using an improved radiative transfer model and tabulated the improved solar irradiance data [Peterson (1976); Demerjian et al. (1980)]. Rate constants have been calculated for NO_2, O_3, HONO, $HONO_2$, CH_2O, CH_3CHO, and H_2O using the updated J_λ values of Peterson [Schere and Demerjian (1977)].

I.B.2. Screening Test Method

A simple first-tier screening test has been developed using equation 9. As an approximation, it is assumed that the reaction quantum yield ϕ_λ is 1, its maximum value.[a] Therefore, the upper limit for direct photoreaction is obtained and equation 9 becomes

$$[k_{dE}]_{max} = 2.303 \sum_\lambda \sigma'_\lambda J_\lambda \qquad (13)$$

Substituting equation 13 in equation 12 yields the lower limit for the half-life

$$[t_{(1/2)E}]_{min} = 0.693\ [k_{dE}]_{max} = 0.301 \sum_\lambda \sigma'_\lambda J_\lambda \qquad (14)$$

The rate constant $[k_{dE}]_{max}$ can be estimated from a knowledge of σ'_λ and J_λ and the use of these parameters in equation 13.

These two parameters can be obtained in the following way.

I.B.2.a. Solar Irradiance

To determine the solar irradiance values (J_λ) , it is necessary to know the solar irradiance at the top of the atmosphere, the absorption due to atmospheric ozone, oxygen, carbon dioxide, water vapor, and aerosols, the molecular scattering (i.e., Raleigh scattering), and the aerosol scattering

[a] Under certain circumstances, the reaction quantum yield can be greater than 1, for example, when a chain reaction occurs after the absorption of a quantum of light. However, this rarely occurs since chemicals are present in the troposphere at very low concentrations.

(i.e., Mie scattering), and surface reflection. Leighton originally estimated J_λ based on limited information [Leighton and Perkins (1956), Leighton (1961)].

Since the research work of Leighton became outdated, Peterson (1976) carried out research (1) to update the radiative transfer model of Leighton; (2) to develop a computer program to calculate solar irradiance (J_λ) from 290 to 700 nm as a function of the solar zenith angle (z) from 0° to 86°; and (3) to input into the computer program the best available atmospheric data on molecular scattering, ozone absorption, aerosol scattering and absorption, absorption by water vapor, oxygen, and carbon dioxide, and the earth's surface albedo as a function of wavelength.

For all the calculations, Peterson used the radiative transfer model first developed by Dave (1972) and improved by Braslau and Dave (1973a,b). This model was used to calculate the optical properties of aerosols.

The Dave model (1972) was designed to calculate radiative fluxes from a flat, horizontal, surface (F_λ). However, for photochemical applications, the irradiance (J_λ) is spherical since the incident radiation enters the polluted layer from all directions. Peterson showed that $J_\lambda = 2F_\lambda$ so that the spherical irradiance is composed of the sum of the upward and downward components. Thus, Peterson modified the Dave model to include the upward and downward components of the flux F_λ.

The ozone absorption coefficients used by Peterson were similar to those used by Leighton (1961). However, Peterson used the value of (O_3) = 0.295 cm, based on the latest ozone measurements, rather than the value of 0.22 cm used by Leighton (1961).

The atmospheric aerosols were assumed (1) to be spherical and homogeneous; (2) to have a given size distribution and known refractive index, both of which were assumed to be independent of the height and wavelength; (3) to have density (i.e., the number of aerosols per unit volume) that could be varied with the height; and (4) to be partly absorbing.

Peterson used the best available data on molecular (i.e., Raleigh) scattering and included absorption by water vapor, oxygen, and carbon dioxide. Finally, the best available surface albedo factors were used to account for reflection from the earth's surface as a function of wavelength.

All of the above data were used in the computer program to calculate the solar irradiance, (J_λ), in photons cm^{-2} s^{-1} for clear sky conditions, for 10 solar zenith angles (0, 10, 20,....., 70, 78, and 86°), and for 48 spectral wavelength intervals from 290 to 700 nm to give the best values of J_λ.

Schere and Demerjian (1977) improved the work of Peterson by calculating J_λ over 10 nm intervals from 290 to 700 nm and expanded the wavelength region from 700 to 800 nm.

The J_λ data obtained by Peterson are instantaneous values in photons cm^{-2} s^{-1}. Because many chemicals require more than one day to photoreact, Hendry [Hendry and Kenley (1979) and in

Mill et al. (1982)] modified J_λ as follows. The J_λ data from the computer program of Schere and Demerjian (1977) were integrated over a 24-hour day to obtain values in photons cm^{-2} d^{-1}. Hendry prepared tables of J_λ as a function of λ in the spectral region 290 to 800 nm in 31 intervals at 10°, 30°, and 50° North latitude for the winter and summer solstices and the equinox. In addition, these tables included J_λ for averaged spring/summer and fall/winter. These tables have been incorporated into a screening test method for determining direct photoreaction rate constants and half-lives for the gas-phase photoreaction of chemicals in sunlight in the environment in the continental United States. The method was updated in 1983 to include tables of J_λ from 20° to 50°N. latitude in 10° increments {Leifer [USEPA (1983)]}.

Recently, Mill et al. (1985) and Davenport (1985) updated the J_λ data of Hendry [Hendry and Kenley (1979) and in Mill et al. (1982)] for the wavelength region 290 to 800 nm in 10-nm intervals. Tables of J_λ were prepared for 0 to 70° North latitude in 10° increments for the winter and summer solstices, the equinox, and the spring/summer and fall/winter averages. The tables corresponding to 20°, 30°, 40°, and 50° N. latitude have been incorporated into a screening test for determining rate constants and half-lives for the gas-phase photoreaction of chemicals in sunlight in the environment {Leifer [USEPA (1985)]}. To make the solar irradiance data complete, Tables of J_λ for 0°, 10°, 60°, and 70° N. latitude have been incorporated

in this report so that the screening test method is applicable to other parts of the United States (e.g., Alaska, Hawaii, etc).

I.B.2.b. Determination of the Cross Section of a Chemical in the Gas-Phase

The cross section of a test chemical can be obtained from the Beer-Lambert law and the ultraviolet-visible absorption spectrum. The Beer-Lambert law states that for an absorbing chemical present in the gas-phase, the decrease in intensity of light with thickness $(-dI/d\ell)_\lambda$, at a fixed wavelength λ, is proportional to the intensity I in photons cm^{-2} s^{-1} and the concentration of the chemical C in the gas-phase [Prutton and Maron (1951)]. Therefore,

$$-(dI/d\ell)_\lambda = \sigma_\lambda C I_\lambda \qquad (15)$$

where σ_λ is the proportionality constant.

Equation 15 can be easily integrated to give the Beer-Lambert equation

$$\ln(I_o/I)_\lambda = \sigma_\lambda C \ell \qquad (16)$$

where ℓ is the thickness of the gas absorption cell in cm; I_o is the intensity of the light at λ and $\ell = 0$; I is the intensity of light at λ and at thickness ℓ; C is the concentration of the gas in molecules cm^{-3}; and σ_λ is the Naperian cross section in the units cm^2 $molecule^{-1}$ (the symbol conventionally used by most atmospheric chemists). Conversion of

equation 16 to the decadic logarithm system yields

$$\log_{10}(I_o/I)_\lambda = \sigma'_\lambda C \ell \qquad (17)$$

where $\sigma'_\lambda = \sigma_\lambda / 2.303$. Since A_λ, the absorbance (which is measured directly on most double beam UV-visible absorption spectrophotometers) is equal to $\log_{10}(I_o/I)_\lambda$, equation 17 becomes

$$A_\lambda = \sigma'_\lambda C \ell \qquad . \qquad (18)$$

The absorbance A_λ over the wavelength interval $\Delta\lambda$, centered at λ, can be obtained from the ultraviolet-visible absorption spectrum of the test chemical in the gas-phase as described by Hendry [Mill et al. (1982)] and improved by Pitts et al. (1981). These data will be used in equation 18 to calculate the cross section for 10 nm wavelength intervals, centered at λ, where the test chemical absorbs light. The method outlined in PART II. of this report is a typical standard spectroscopic procedure for determining the cross section of chemicals in the gas-phase.

I.B.3. Applicability and Specificity

This test method is applicable to all chemicals which have UV-visible absorptions in the range 290-800 nm. Solar radiation reaching the earth's surface has a sharp cutoff at a wavelength of approximately 290 nm due to the absorption by ozone [Leighton (1961), Peterson (1976), Zepp and Cline (1977), Demerjian

(1980)]. The long wavelength limit is set by thermochemistry since light of wavelength greater than 800 nm is not of sufficient energy to break chemical bonds of ground state molecules [Calvert and Pitts (1966), Benson (1976)]. Direct photoreaction does not occur unless there is absorption of radiant energy. This is a direct consequence of the Grottus-Draper law, the first law of photochemistry. If a chemical in the gas-phase only absorbs light at wavelengths below 290 nm it will not undergo direct photoreaction in sunlight. A few examples of chemicals that only absorb light below 290 nm and need not be tested in this test guideline are alkanes, alkenes, alkynes, dienes, and fluoroalkanes.

This test guideline is only applicable to pure chemicals and not to the technical grade. Overestimates of cross sections usually occur when technical grade substances are tested because the impurities frequently absorb in the same spectral region as the pure chemical.

This first-tier screening test can be employed to estimate $[k_{dE}]_{max}$ and $[t_{(1/2)E}]_{min}$ as a function of latitude and season of the year in the United States including Alaska, Hawaii, etc. under clear sky conditions. These data are in a form suitable for mathematical modeling for the environmental fate of a test chemical. Since σ'_λ can be determined relatively easily and cheaply by spectroscopic techniques and tables of J_λ are readily available, $[k_{dE}]_{max}$ and $[t_{(1/2)E}]_{min}$ can be obtained easily and cheaply.

If the data obtained from this test guideline indicate that gas-phase photoreaction is an important process relative to other gas-phase transformation processes such as oxidation with OH and O_3, then it is recommended that an upper-tier photoreaction test be carried out to determine the reaction quantum yield ϕ_λ and thus obtain more precise environmentally relevant rate constants and half-lives.

PART II. TEST PROCEDURES AND DATA REPORTING

II.A. Procedures

The procedures outlined in this test guideline are based on the method proposed by Hendry [Hendry and Kenley (1979) and in Mill et al. (1982)] and developed by Pitts et al. (1981). It is also recommended that Test Guideline CG-1050, Absorption in Aqueous Solution: Ultraviolet/Visible Spectra [USEPA (1985)] be consulted for additional guidance.

II.A.1. Experimental Conditions

II.A.1.a. Ultraviolet-Visible Spectrophotometer

Although single-beam spectrophotometers may be used, recording double-beam spectrophotometers are highly recommended. It is extremely important that the spectrophotometer be able to scan over the wavelength region 270 to 800 nm and have an absorbance sensitivity, at a signal/noise ratio of 1, of approximately 0.001. It is important that the spectrophotometer be able to attain a 90 percent separation of two monochromatic spectral

features approximately 4 nm apart, peak to peak (i.e., the resolution should be at least 4 nm). It is also desirable to have a spectrophotometer that can accomodate absorption cells of length > 10 cm. A Cary 219 UV-Visible Spectrophotometer, or an equivalent model, is highly recommended.

II.A.1.b. Vapor and Liquid Absorption Cells

Long path length cells are preferable; however, many commercial spectrophotometers will only accept absorption cells of 10 cm or less. A suitable vapor cell is depicted in Figure 1 [which was reproduced from the report by Pitts et al. (1981)] and can be contructed as follows. The vapor cell should be constructed of Pyrex, 1 cm o.d. and 10 cm in length, and be fitted with plane parallel quartz windows at each end. The quartz windows can be conveniently attached to the Pyrex cell with vacuum tight epoxy resin (e.g., Torr-Seal, Varian Associates) only applied to the outside surface. A Teflon stopcock (or a Pyrex "o" ring stopcock) should be connected to the cell and contain an "o"-ring joint. The "o"-ring joint (e.g., #7 or #9, Kontes or Ace Glass) must match the one on the vacuum rack. Viton "o"-rings are highly recommended and should be frequently inspected for signs of deterioration which would result in vacuum leaks. A matched reference cell is extremely useful but not essential. However, the sample and reference cells should be very similar. Small spectral differences between the cells can be compensated for by running a blank with the sample and reference cells in the

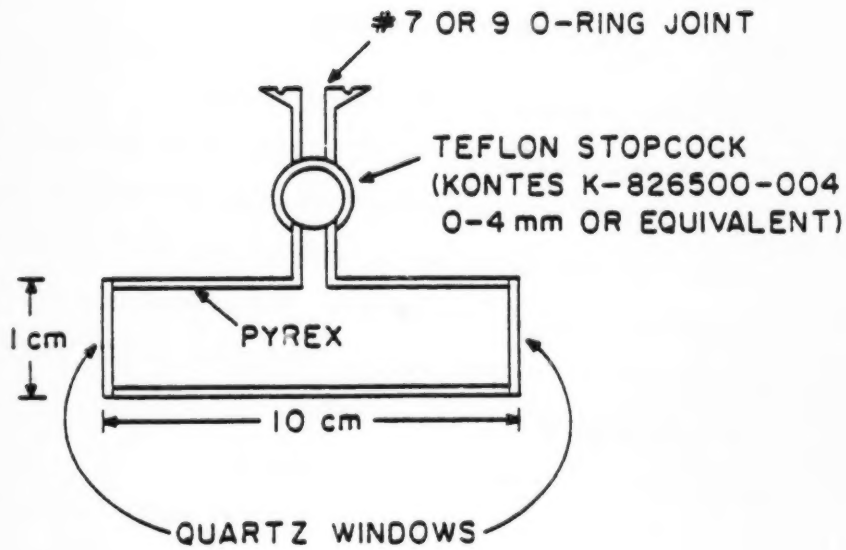


Figure 1. Gas Absorption Cell [Reproduced from Pitts et al. (1981).]

spectrophotometer. The use of stopcock grease is not required with these cells and should be avoided.

A matched pair of liquid absorption cells is very desirable but is not essential. A pair of quartz ultraviolet absorption cells, 10 cm in length, and containing ground glass or Teflon stoppers are recommended. These liquid absorption cells are readily available commercially.

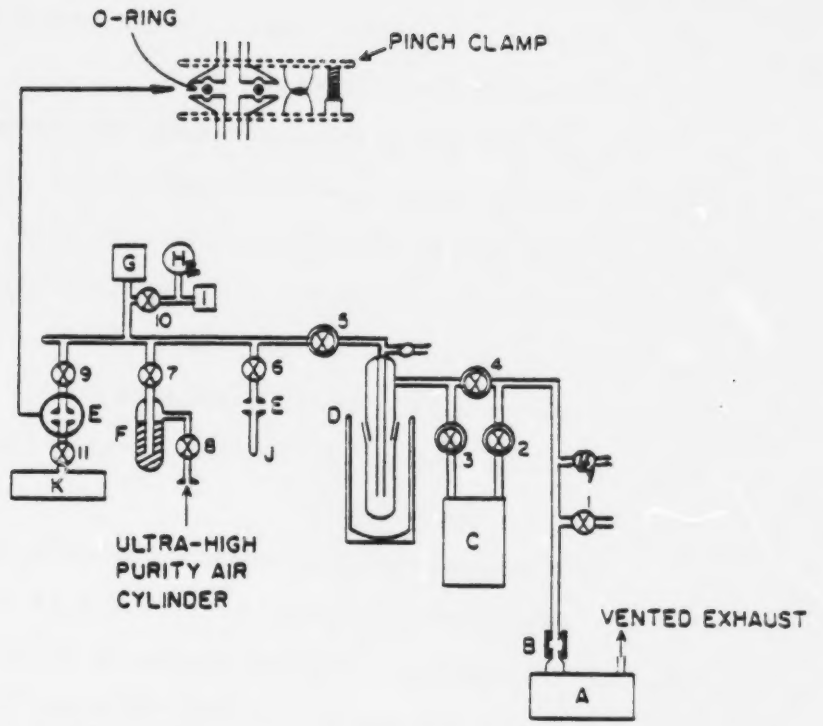
II.A.1.c. Vacuum Gas Handling System

A suitable gas handling system is shown diagrammatically in Figure 2 [which was reproduced from the report by Pitts et al. (1981) and was modified slightly] and should be constructed completely with Pyrex glass. The components of the gas handling system are discussed below. The use of stopcock grease is not required and should be avoided.

II.A.1.c.i. Vacuum Pumping System

In order to achieve a good vacuum, i.e., pressures $<10^{-5}$ torr ($<1.3 \times 10^{-6}$ kPa), two pumps are required. The forepump (A) must be capable of achieving a pressure <0.05 torr (<0.0065 kPa). A rotary pump (e.g., a Welch Model 1402 Duo-Seal or an equivalent model) is recommended. The forepump can be attached to the vacuum system by means of heavy-walled rubber vacuum tubing (B), or any flexible vacuum tubing. The exhaust from this pump should be vented into a hood.

The second pump, a high vacuum model, should be a multi-stage oil diffusion pump (C) [e.g., a Consolidated Vacuum Corp.



A ROTARY PUMP
B RUBBER TUBING (THICK WALLED)
C DIFFUSION PUMP
D TRAP AT LIQUID NITROGEN TEMPERATURE
E #7 OR 9 O-RING JOINTS
F MOLECULAR SIEVE 4A TRAP
G CAPACITANCE MANOMETER
H THERMOCOUPLE GAUGE
I IONIZATION GAUGE
J LIQUID RESERVOIR
K GAS ABSORPTION CELL

⊗ 0-4 OR 0-5 mm STOPCOCKS

⊗ 0-8 OR 0-10 mm STOPCOCKS

Figure 2. Schematic of Gas Handling Vacuum Rack [Reproduced from Pitts et al.[3] (1981) and modified slightly.]

VMF-10 or VMF-20 or an equivalent model]. The pump fluid should be a silicone oil with a room temperature vapor pressure of 10^{-6} torr (1.3×10^{-7} kPa) [e.g., Dow-Corning D.C. 702 or 703, or an equivalent grade].

It is extremely important that the pumping system contain a trap (D) cooled with liquid nitrogen. The cone and socket joint on this trap can be conveniently sealed with Apiezon W wax, or an equivalent grade. This wax only requires gentle heating to apply and makes an effective vacuum seal. It is possible that a few test chemicals could dissolve Apiezon W wax. In this case, an inert silicone grease may be used to seal the trap.

II.A.1.c.ii. Vacuum Rack

The recommended vacuum rack assembly is depicted in Figure 2. All stopcocks should be of Teflon with Viton "o"-rings [Kontes K-826500 or K-826510 series or equivalent grades (or Pyrex "o" ring stopcocks)]. The "o"-ring joints (E) [#7 or #9] must be compatible with those on the gas absorption cell (K) or on the liquid reservoir (J). These "o"-ring joints should be clamped by pinch clamps with a screw lock device (e.g., Thomas #18A, or an equivalent grade).

II.A.1.c.iii. Pressure Gauges

Three pressure gauges are required:

(1) An ionization gauge to measure high vacuum [$<10^{-3}$ torr ($<1.3 \times 10^{-4}$ kPa)];

(2) a thermocouple gauge to monitor the pressure in the range 10^{-3} to 1 torr (1.3×10^{-4} to 0.13 kPa). A convenient

pressure monitoring system which contains ionization and thermocouple gauges is a Consolidated Vacuum Corp. Model GIC-300A or an equivalent model; and

(3) a pressure gauge to monitor the pressure of the test chemical and diluent in the range 0.01 to 760 torr (0.0013 to 101.3 kPa); for example, an MKS Baratron 310 BHS-1000 with the associated 170-6C electronics unit and a digital readout or an equivalent model. While this vacuum gauge exhibits a slow zero drift, it can be readily rezeroed using the ionization gauge when the pressure is approximately 10^{-3} torr (0.00013 kPa) or less.

II.A.2. Operation of the Gas Handling System

Since there are a wide variety of procedures available for operating a gas handling system, the method used is left to the discretion of the tester. For those testers who do not have experience in handling a vacuum system, the detailed procedure described in Appendix B is highly recommended.

II.A.3. Preparation of Samples

II.A.3.a. Preparation of the Gas-Phase Test Chemical Sample: Preliminary Steps

If the test chemical is a gas at room temperature, then attach the gas container to the "o"-ring at the point where the liquid reservoir (J) is placed. Close stopcocks 2 and 3 and open 4. Pump until the pressure is less than 10^{-2} torr ($<1.3 \times 10^{-3}$ kPa) as read on thermocouple gauge (H_2). Then open stopcocks 2 and 3 and close 4 and pump until the pressure is less than 10^{-5} torr ($<1.3 \times 10^{-6}$ kPa) as read on the ionization gauge (I).

If the test chemical is a liquid at room temperature, add a few cubic centimeters of liquid to a reservior tube (J), sealed at one end and containing an "o"-ring at the other end, and connect the tube via the "o"-ring to stopcock 6. Freeze the sample with a Dewar containing liquid nitrogen, close stopcocks 2 and 3 and open 4 and 6. Degas the test chemical by allowing it to warm up to the liquid state, briefly degas, and refreeze the liquid. Repeat this process three or more times until the evolution of gas bubbles ceases upon thawing. Freeze the liquid, open stopcocks 2 and 3 and close 4. Pump until the pressure is less than 10^{-5} torr ($<1.3 \times 10^{-6}$ kPa) as indicated by the ionization gauge (I). Close stopcock 6.

II.A.3.b. Introduction of the Test Chemical into the Gas Absorption Cell

For introduction of the test chemical into the gas absorption cell, close stopcocks 5, 7, and 10, with 9 and 11 open. If the test chemical is a gas, then stopcock 6 should be opened and the gas container valve gradually opened to admit the gas into the gas handling manifold and gas absorption cell until the desired pressure is attained, as read on the capacitance manometer (G). Close the gas container valve and stopcock 6 and allow approximately 5 minutes before the final pressure at (G) is read. If the pressure has not stabilized in approximately 5 minutes, allow the cell to condition for several hours before the final pressure at (G) is read.

For a liquid chemical in the reservoir (J), which has been degassed and is at liquid nitrogen temperature, the liquid nitrogen Dewar should be removed and stopcock 6 opened. The cold liquid in the reservoir (J) is allowed to warm up until the required pressure is attained, as read by the capacitance manometer (G). Close stopcock 6 and cool the reservoir again with liquid nitrogen and allow approximately 5 minutes before the final pressure at (G) is read. If the pressure has not stabilized in approximately 5 minutes, allow the cell to condition for several hours before the final pressure at (G) is read.

With stopcocks 6, 8, and 11 closed and 5, 7, 9, and 10 open, the gas handling manifold is evacuated as described previously to a pressure less than 10^{-5} torr ($<1.3 \times 10^{-6}$ kPa). Stopcocks 5 and 10 are then closed and ultrahigh purity air from a cylinder is admitted into the gas handling manifold via stopcock 8 and through the trap (F) containing Molecular Sieve 4A. When the manifold is at 1 atmosphere pressure, as measured by pressure gauge (G), stopcock 11 is briefly opened to pressure the gas absorption cell to 1 atmosphere, and then closed. Stopcocks 8 and 9 are closed and the gas handling system is evacuated as described previously. The gas absorption cell can then be removed from (E) and covered to avoid photoreaction.

Based on the pressure P of the test chemical, as measured by gauge (G), the concentration of the gas sample is

$$C \text{ (molecules cm}^{-3}) = 9.657 \times 10^{18} \text{ P(torr)/T(K)} \quad (19)$$

$$C \text{ (molecules cm}^{-3}) = 1.287 \times 10^{18} \text{ P(kPa)/T(K)} \quad (20)$$

where T is the room temperature in K, which should be routinely monitored with a thermometer.

The recommended pressure of the test chemical should be in the range 1-5 torr (0.13-0.65 kPa) where the Beer-Lambert law is obeyed. A final check on whether the test chemical obeys the Beer-Lambert law can be accomplished by demonstrating the constancy of the cross section at three partial pressures differing by a factor of 10.

II.A.3.c. Preparation of Solution-Phase Test Chemical Sample

If the properties of the test chemical (i.e., small cross sections, low vapor pressure) are such that the maximum absorbance obtainable is one-tenth of the most sensitive spectrophotometer scale or less (i.e., 0.001 absorbance), a solution-phase study should be undertaken. The most sensitive scale may be limited by inherent spectrophotometer noise. For example, a given spectrophotometer's most sensitive scale is 0.00 to 0.10 absorbance units. Therefore, a test chemical for which the product of its maximum cross section and its concentration is less than 0.001 (in a 10 cm cell) could not be analyzed in the vapor phase with this particular spectrophotometer.

The following spectroscopic grade chemicals are recommended to prepare solutions: n-hexane, and cyclohexane. Solutions of

up to 10 percent by volume of test chemical can be prepared in one of these solvents in the standard manner.

The concentration of the test chemical is given by the equations

$$C \text{ (molecules cm}^{-3}) = 6.022 \times 10^{23} \text{ mass (g)/FW } (V_d) \qquad (21)$$

$$C \text{ (molecules cm}^{-3}) = 6.022 \times 10^{23} \; V_s \rho / \text{FW } (V_d) \qquad (22)$$

where V_s is the volume of test chemical delivered into a volume V_d of solvent in cm^3, FW is the formula weight of the test chemical in g, and ρ is the density of the test chemical in g cm^{-3} at the room temperature the solution was prepared.

II.A.4. Procedure for Obtaining the Spectrum

As a general guide to obtaining UV-visible absorption spectra, the procedures outlined in Test Guideline CG-1050, Absorption in Aqueous Solution: Ultraviolet/Visible Spectra, are highly recommended. Since the method presented in this procedure was developed by Pitts et al. (1981), it is highly recommended that this report be consulted for further details.

II.A.4.a. Determination of the Cell Path Length

The method for determining the cell path length of gas or liquid cells is left to the discretion of the tester. However, the method listed in Test Guideline CG-1050 {Leifer [USEPA (1985)]}, using one of their reference compounds, is highly recommended.

II.A.4.b. Gas-Phase Spectrum

Measure the absorbance of the test chemical in duplicate relative to a matched cell filled with ultrahigh purity air from the same cylinder similarly passed through trap (F) containing the molecular sieve. The absorbance should be measured at wavelengths $\lambda > 280$ nm using minimum slit widths. Record, in duplicate, the baseline when both the sample and reference cells are only filled with high purity air dried through the molecular sieve and at the same settings as used for the test chemical sample. These data will be used to calculate the cross section, σ'_λ, at the appropriate wavelength intervals, centered at wavelength λ, listed in Tables 3-10, Appendix A.

II.A.4.c. Solution-Phase Spectrum

Measure the absorbance of the test chemical in duplicate relative to a matched cell containing the solvent. The absorbance should be measured for wavelengths $\lambda > 280$ nm using the minimum slit widths. Record, in duplicate, the baseline when both the sample and reference cells are filled with the solvents. These data will be used to calculate the cross sections, σ'_λ, for the appropriate wavelength intervals, centered at λ, listed in Tables 3-10, Section A.

The concentration of the test chemical should be in the range where the Beer-Lambert law is obeyed. A check on whether the test chemical obeys this law can be accomplished by demonstrating the constancy of the cross section at three concentrations differing by a factor of 10.

II.B. Data and Reporting

II.B.1. Treatment of Results

II.B.2. Determination of the Cross Section from the Gas-Phase Spectrum

The cross section, σ'_λ, can be determined from the gas-phase absorption spectrum and the Beer-Lambert law in the form

$$\sigma'_\lambda = A_\lambda / C \ell \qquad (23)$$

where A_λ is the absorbance at wavelength λ, centered in the wavelength interval $\Delta\lambda$, C is the concentration of test chemical in molecules cm^{-3}, and ℓ is the cell path length in cm. The cross section of the test chemical should be determined for the wavelength intervals listed in Tables 3-10, Appendix A.

There are at least three nondestructive methods of determining the absorbance over a specified wavelength interval: estimation, square counting, and planimetry. For many spectra, estimating an average absorbance over a small wavelength interval is sufficient to yield accurate results. However, for spectra containing rapidly changing absorptions and complex fine structure, square counting or planimetry should be used. These two methods require the integration of a definite region (in A_λ x nm) followed by division by the width of the region in nm to obtain the absorbance. The method using a compensating polar planimeter is the most accurate and is highly recommended. The absorbance should be obtained from the average of three tracings.

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II.B.3. Determination of the Cross Section from the Solution-Phase Spectrum

The cross section, σ'_λ , can be determined from the solution-phase spectrum using equation 23 for the wavelength intervals listed in Tables 3-10, Appendix A. For solution spectra, estimating an average absorbance over the wavelength intervals is sufficient to yield accurate results.

II.B.4. Estimation of the Maximum Direct Photoreaction Rate Constant and Minimum Half-Life in the Gas-Phase

Using the cross sections obtained from the spectra and the values of J_λ from Tables 3-10, Appendix A, the maximum direct photoreaction rate constant $[k_{dE}]_{max}$ can be calculated at a specific latitude and season of the year using equation 13. The minimum half-life $[t_{(1/2)E}]_{min}$ can be calculated using this $[k_{dE}]_{max}$ in equation 14.

An example is presented in PART III. to illustrate how the test data obtained in this test guideline is used.

II.B.5. Test Data Report

(a) Submit the original chart, or photocopy, containing a plot of absorbance vs. wavelength plus the baseline. Spectra should include a readable wavelength scale, preferably marked at 10 nm intervals. Each spectrum should be clearly marked.

(b) Gas-Phase Spectra

(i) Report the pressure of the test chemical in torr (or kPa), the concentration in molecules cm^{-3}, and the path length of the sample cell in cm. Describe the method used to determine the path length and report the experimental data.

(ii) Report the wavelength λ, the wavelength interval for each 10 nm over the region of absorption, the value of the absorbance (A_λ) for each replicate, the mean absorbance, and the mean cross section in cm^2 $molecule^{-1}$.

(iii) Report the site (or sites) where the chemical is manufactured.

(iv) Report the estimated maximum direct photoreaction rate constant in d^{-1} and the corresponding minimum half-life in days at the site (or sites) where the chemical is manufactured for the summer and winter solstices.

(c) Solution-Phase Spectra

(i) Report the concentration of the test chemical in molecules cm^{-3}, the type of cell used (quartz or borosilicate), and the path length in cm. Describe the method used to determine the path length and report the experimental results.

(ii) Report the identity of the solvent.

(iii) Report the wavelength λ, the wavelength interval over the region of absorption, the value of the absorbance (A_λ) of each replicate, the mean absorbance, and the mean cross section (σ'_λ) in cm^2 $molecule^{-1}$.

(iv) Report the estimated maximum direct photoreaction rate constant in d^{-1} and the corresponding minimum half-life in days at the site (or sites) where the chemical is produced for the summer and winter solstices.

(d) Report the name, structure, and purity of the test chemical.

(e) Submit a recent spectrum on appropriate reference chemicals for photometric and wavelength accuracy.

(f) Report the name and model of the spectrophotometer used.

(g) Report the various control settings employed with the spectrophotometer. These might include scan speed, slit width, given, etc.

(h) Report anything unusual about the test; e.g., if the Beer-Lambert law is not obeyed at a pressure of 1-5 torr (0.13 to 0.65 kPa), report the pressure at which the deviation was overcome and the experimental data. If the Beer-Lambert law is not obeyed in solution at high concentrations, report the concentration at which the deviation was overcome and the experimental data.

(i) Report any other relevant information.

PART III. ILLUSTRATIVE EXAMPLE

Consider a chemical plant located in Freeport, TX which produces acrolein [CH_2=CHCHO] continuously every day of the year. Despite the fact that all acrolein wastes, including vented vapors, are treated in a waste treatment plant, some acrolein escapes into the atmosphere. The chemical plant is located at 29° N. latitude. Estimate the maximum sunlight direct photoreaction rate constant and the corresponding minimum half-life in the troposphere in the vicinity of the plant for the winter and summer solstices under clear sky conditions.

The vapor phase spectrum of acrolein was obtained by the procedure outlined in this test guideline and is depicted in

Figure 3.[b] The path length of the sample gas absorption cell was measured according to the recommended procedure and was found to be 9.98 cm. The gas absorption cell contained 6.52×10^{16} molecules cm^{-3} of acrolein. A compensating polar planimeter was used to integrate each 10 nm interval throughout the region of absorption from 285 nm to 425 nm in both the sample and blank spectra. Based on triplicate measurements, one square, corresponding to 0.001 absorbance units (A), was found to be 0.148 vernier units (v.u.). The mean absorbance (A_λ) was obtained from these spectra and the mean cross section (σ'_λ) was obtained using equation 23 for each wavelength interval, centered at λ . All the results are summarized in Table 1.

A sample calculation is given for the wavelength λ = 350 nm centered over the wavelength interval 345-355 nm. For convenience, the area A, corresponding to 100 squares was blocked off in this absorption area (Figure 3) and was not integrated with the planimeter. The average vernier reading of the remaining absorption area was 7.2 v.u. Hence,

$$\frac{7.2 \text{ v.u.}}{0.148 \text{ v.u./square}} = 49 \text{ squares}$$

and the total area in the spectrum in the wavelength interval 345-355, centered at λ = 350 nm, is 149 squares. This number of squares corresponds to 0.0149 absorbance units:

$$\frac{(149 \text{ squares})(0.001 \text{ A/square})}{10} = 0.0149 \text{ A}$$

[b] The spectral data were taken from the work of Pitts et al. (1981).

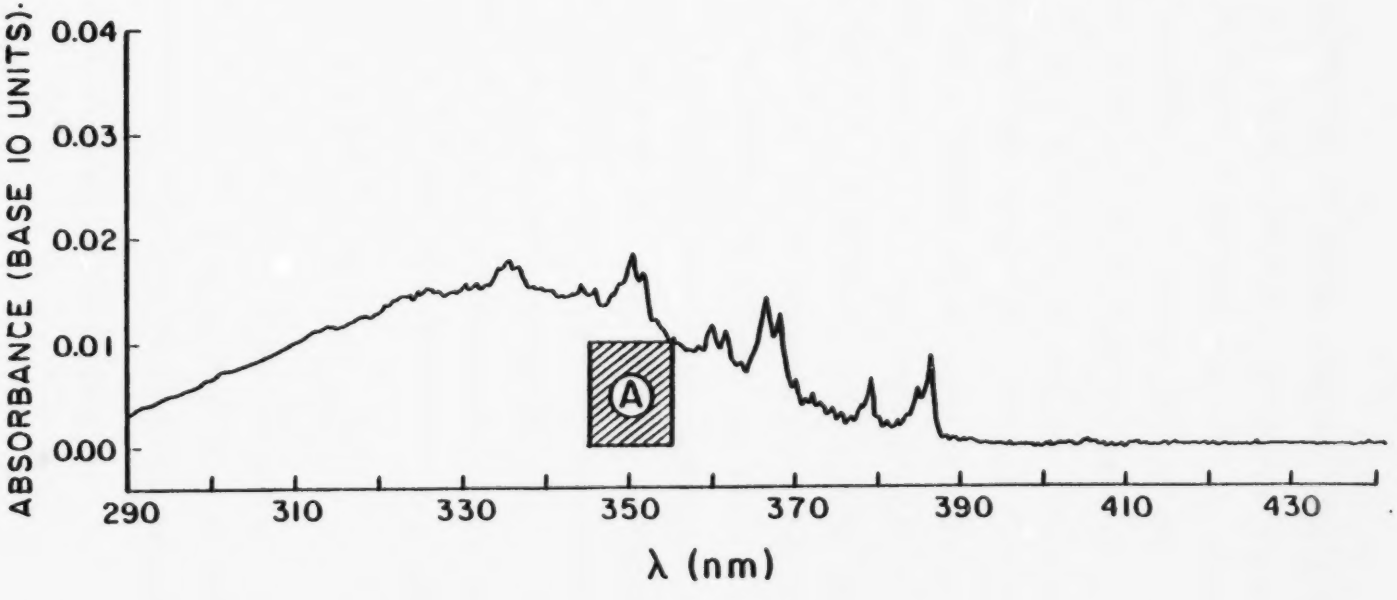

Figure 3. Gas Phase Absorption Spectrum of Acrolein [Reproduced from Pitts et al. (1981).]

TABLE 1. ABSORBANCE AND CROSS SECTION FOR ACROLEIN VAPOR*

Wavelength λ (nm)	Wavelength Interval (nm)	Mean Absorbance [A_λ]	Mean Cross Section [σ'_λ] (cm^2 $molecule^{-1}$)
290	285-295	0.0037	5.69×10^{-21}
300	295-305	0.0066	1.01×10^{-20}
310	305-315	0.0104	1.60×10^{-20}
320	315-325	0.0137	2.11×10^{-20}
330	325-335	0.0156	2.40×10^{-20}
340	335-345	0.0156	2.40×10^{-20}
350	345-355	0.0151	2.32×10^{-20}
360	355-365	0.0096	1.48×10^{-20}
370	365-375	0.0073	1.12×10^{-20}
380	375-385	0.0031	4.76×10^{-21}
390	385-395	0.0016	2.46×10^{-21}
400	395-405	0.0004	6.15×10^{-22}
410	405-415	0.0003	4.61×10^{-22}
420	415-425	0.0000	0.00

*6.52×10^{16} molecules cm^{-3} in a 9.98 cm gas absorption cell. The data was taken from the report by Pitts et al. (1981).

From the blank spectrum, the baseline absorbance (A_λ blank) over this interval was -0.0001. The sample trace lay at -0.0001 absorbance units relative to a zero point at 450 nm. The observed sample absorbance is then equal to 0.0150 (0.0149 + 0.0001). The absolute corrected absorbance for the sample is given by

$$A^{corr}_{\lambda\ sample} = A^{obs}_{\lambda\ sample} - A_{\lambda\ blank}$$

$$A^{corr}_{\lambda\ sample} = 0.0150 - (-0.001) = 0.0151\ A$$

Using equation 23 and the values for the corrected sample absorbance, ℓ , and C, the mean cross section for the wavelength λ = 350 nm, centered over the wavelength interval 345-355 nm, is

$$\sigma'_\lambda = \frac{0.0151}{6.52 \times 10^{16}\ \text{molecules cm}^{-3}\ (9.98\ \text{cm})}$$

$$\sigma'_\lambda = 2.32 \times 10^{-20}\ \text{cm}^2\ \text{molecule}^{-1}.$$

Since the plant is located at 29° N. latitude, the closest J_λ values are at 30° N. latitude. These values are obtained from Table 6 and are summarized in Table 2 for the summer and winter solstices. Using the data in Tables 1 and 2, the products $\sigma'_\lambda J_\lambda$ are calculated for each wavelength interval, centered at λ , and the results are summarized in Table 2 for each of the

TABLE 2. CALCULATION OF $[k_{dE}]_{max}$ FOR ACROLEIN VAPOR: RATE AT 30° N. ON WINTER AND SUMMER SOLSTICES

		Summer Solstice		Winter Solstice	
Wavelength λ (nm)	Wavelength Interval (nm)	J_λ $\left[\frac{\text{photons}}{\text{cm}^{-2}\text{d}^{-1}}\right]$	$\sigma'_\lambda J_\lambda$ $[\text{d}^{-1}]$	J_λ $\left[\frac{\text{photons}}{\text{cm}^{-2}\text{d}^{-1}}\right]$	$\sigma'_\lambda J_\lambda$ $[\text{d}^{-1}]$
290	285-295	1.0×10^{15}	0.000	2.1×10^{12}	0.000
300	295-305	8.31×10^{17}	0.008	8.35×10^{16}	0.001
310	305-315	1.14×10^{19}	0.182	3.00×10^{18}	0.048
320	315-325	2.84×10^{19}	0.599	1.06×10^{19}	0.224
330	325-335	5.02×10^{19}	1.205	2.13×10^{19}	0.511
340	335-345	5.49×10^{19}	1.318	2.48×10^{19}	0.595
350	345-355	6.28×10^{19}	1.457	2.89×10^{19}	0.671
360	355-365	6.49×10^{19}	0.961	3.10×10^{19}	0.459
370	365-375	8.09×10^{19}	0.906	3.95×10^{19}	0.442
380	375-385	7.93×10^{19}	0.378	3.95×10^{19}	0.188
390	385-395	8.12×10^{19}	0.200	4.12×10^{19}	0.101
400	395-405	1.11×10^{20}	0.068	5.73×10^{19}	0.035
410	405-415	1.41×10^{20}	0.065	7.37×10^{19}	0.034
420	415-425	1.47×10^{20}	0.000	7.81×10^{19}	0.000
			$\sum_\lambda \sigma'_\lambda J_\lambda = 7.34_7$		$\sum_\lambda \sigma'_\lambda J_\lambda = 3.30_4$

solstices. The terms $\sum_{\lambda} \sigma'_{\lambda} J_{\lambda}$ are also listed for each solstice at the bottom of Table 2. Using these data in equations 13 and 14 yields:

Summer	Winter
$[k_{dE}]_{max} = 16.9\ d^{-1}$	$[k_{dE}]_{max} = 7.60\ d^{-1}$
$[t_{(1/2)E}]_{min} = 0.041\ d$	$[t_{(1/2)E}]_{min} = 0.091\ d$

Thus, under the assumption that $\phi_{\lambda} = 1$, acrolein transforms rapidly under clear sky conditions in the vicinity of the plant at Freeport, TX on the summer and winter solstices. To define the rate of direct photoreaction more precisely, ϕ_{λ} must be determined in the laboratory using the procedure outlined in the report by Mill (1983) and in the Test Guideline § 796.3810, to be published shortly.

APPENDICES

Appendix A. Tables 3-10 [from Mill et al. (1985) and Davenport (1985)].

Table 3

J_λ VALUES AT 0°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.00000129	0.0000768	0.00000124	290	0.0000261	0.0000278	290
300	0.0557	0.0754	0.0557	300	0.0654	0.0654	300
310	0.873	1.017	0.873	310	0.945	0.945	310
320	2.28	2.52	2.28	320	2.40	2.40	320
330	4.09	4.44	4.09	330	4.27	4.27	330
340	4.51	4.85	4.51	340	4.68	4.68	340
350	5.11	5.46	5.11	350	5.29	5.29	350
360	5.37	5.72	5.37	360	5.55	5.55	360
370	6.71	7.13	6.71	370	6.92	6.92	370
380	6.60	6.98	6.60	380	6.79	6.79	380
390	6.77	7.14	6.77	390	6.96	6.96	390
400	9.28	9.77	9.28	400	9.53	9.53	400
410	11.8	12.4	11.8	410	12.1	12.1	410
420	12.3	12.9	12.3	420	12.6	12.6	420
430	12.5	13.1	12.5	430	12.8	12.8	430
440	13.9	14.5	13.9	440	14.2	14.2	440
450	16.0	16.7	16.0	450	16.3	16.3	450
460	17.3	18.0	17.3	460	17.7	17.7	460
470	17.8	18.6	17.8	470	18.2	18.2	470
480	18.1	18.8	18.1	480	18.5	18.5	480
490	18.1	18.9	18.1	490	18.5	18.5	490
500	18.4	19.2	18.4	500	18.8	18.8	500
510	18.6	19.3	18.6	510	19.0	19.0	510
520	18.6	19.4	18.6	520	19.0	19.0	520
530	18.8	19.6	18.6	530	19.2	19.2	530
540	18.7	19.4	18.8	540	19.0	19.0	540
550	18.6	19.3	18.7	550	19.0	19.0	550
560	18.8	19.5	18.8	560	19.2	19.2	560
570	19.0	19.8	19.0	570	19.4	19.4	570
580	19.4	20.2	19.4	580	19.8	19.8	580
590	19.7	20.4	19.7	590	20.1	20.1	590
600	19.8	20.6	19.8	600	20.2	20.2	600
610	20.0	20.7	20.0	610	20.4	20.4	610
620	19.9	20.7	19.9	620	20.3	20.3	620
630	19.8	20.7	19.8	630	20.3	20.3	630
640	20.3	21.2	20.4	640	20.8	20.8	640
650	20.9	21.7	20.9	650	21.3	21.3	650
660	21.2	22.0	21.2	660	21.6	21.6	660
670	21.5	22.2	21.5	670	21.9	21.9	670
680	21.5	22.2	21.5	680	21.9	21.9	680
690	21.5	22.2	21.5	690	21.9	21.9	690
700	21.4	22.2	21.4	700	21.8	21.8	700
710	21.3	22.0	21.3	710	21.7	21.7	710
720	21.2	21.9	21.2	720	21.5	21.5	720
730	21.0	21.8	21.0	730	21.4	21.4	730
740	20.9	21.5	20.9	740	21.3	21.3	740
750	20.8	21.5	20.8	750	21.2	21.2	750
760	20.7	21.4	20.7	760	21.0	21.0	760
770	20.5	21.2	20.5	770	20.9	20.9	770
780	20.4	21.1	20.4	780	20.8	20.8	780
790	20.3	21.0	20.3	790	20.6	20.6	790
800	20.2	20.8	20.2	800	20.5	20.5	800

[a] J_λ values are in units of 10^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Table 4

J_λ VALUES AT 10°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.0000316	0.0000542	0.00000235	290	0.00000879	0.0000589	290
300	0.0713	0.0718	0.0381	300	0.0517	0.0742	300
310	1.01	0.992	0.698	310	0.823	1.02	310
320	2.55	2.48	1.934	320	2.17	2.55	320
330	4.52	4.39	3.55	330	3.91	4.51	330
340	4.95	4.79	3.96	340	4.32	4.93	340
350	5.58	5.41	4.51	350	4.89	5.56	350
360	5.85	5.66	4.76	360	5.15	5.82	360
370	7.30	7.06	5.98	370	6.44	7.26	370
380	7.16	6.92	5.89	380	6.33	7.11	380
390	7.33	7.08	6.07	390	6.50	7.28	390
400	10.0	9.70	8.34	400	8.92	9.97	400
410	12.8	12.3	10.6	410	11.4	12.7	410
420	13.3	12.8	11.1	420	11.9	13.2	420
430	13.5	13.0	11.3	430	12.1	13.4	430
440	14.9	14.4	12.6	440	13.3	14.8	440
450	17.2	16.6	14.5	450	15.4	17.0	450
460	18.6	17.9	15.7	460	16.6	18.4	460
470	19.1	18.5	16.2	470	17.2	19.0	470
480	19.4	18.7	16.5	480	17.4	19.2	480
490	19.5	19.0	16.5	490	17.5	19.3	490
500	19.8	19.1	16.8	500	17.8	19.6	500
510	19.9	19.2	16.9	510	17.9	19.8	510
520	20.0	19.3	17.0	520	17.9	19.8	520
530	20.2	19.4	17.1	530	18.1	20.0	530
540	20.0	19.3	17.0	540	18.0	19.8	540
550	20.0	19.2	17.0	550	17.9	19.8	550
560	20.1	19.4	17.1	560	18.1	19.9	560
570	20.4	19.7	17.4	570	18.3	20.2	570
580	20.9	20.1	17.7	580	18.7	20.7	580
590	21.1	20.3	17.9	590	18.9	20.9	590
600	21.2	20.5	18.1	600	19.1	21.0	600
610	21.4	20.6	18.2	610	19.2	21.2	610
620	21.4	20.6	18.1	620	19.1	21.2	620
630	21.4	20.6	18.0	630	19.1	21.2	630
640	21.9	21.1	18.6	640	19.6	21.7	640
650	22.4	21.5	19.1	650	20.1	22.1	650
660	22.7	21.8	19.4	660	20.4	22.5	660
670	23.0	22.1	19.6	670	20.7	22.7	670
680	23.0	22.1	19.7	680	20.7	22.7	680
690	23.0	22.1	19.7	690	20.7	22.7	690
700	22.9	22.0	19.7	700	20.7	22.7	700
710	22.8	21.9	19.6	710	20.5	22.5	710
720	22.6	21.8	19.5	720	20.4	22.4	720
730	22.5	21.6	19.3	730	20.3	22.3	730
740	22.4	21.5	19.2	740	20.2	22.1	740
750	22.2	21.4	19.1	750	20.1	22.0	750
760	22.1	21.3	19.0	760	20.0	21.9	760
770	22.0	21.1	18.9	770	19.8	21.7	770
780	21.8	21.0	18.8	780	19.7	21.6	780
790	21.7	20.9	18.7	790	19.6	21.4	790
800	21.6	20.7	18.6	800	19.5	21.3	800

[a] J_λ values are in units of 10^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Table 5

J_λ VALUES AT 20°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.0000811	0.00000131	0.000000108	290	0.000000896	0.0000625	290
300	0.0810	0.0611	0.0212	300	0.0359	0.0769	300
310	1.10	0.9148	0.499	310	0.663	1.05	310
320	2.74	2.35	1.52	320	1.855	2.62	320
330	4.82	4.20	2.90	330	3.42	4.63	330
340	5.27	4.61	3.28	340	3.82	5.06	340
350	5.94	5.22	3.77	350	4.36	5.71	350
360	6.22	5.47	4.01	360	4.61	5.98	360
370	7.76	6.84	5.06	370	5.79	7.46	370
380	7.60	6.71	5.02	380	5.71	7.31	380
390	7.77	6.88	5.19	390	5.88	7.48	390
400	10.6	9.44	7.17	400	8.10	10.2	400
410	13.5	12.0	9.17	410	10.3	13.0	410
420	14.1	12.5	9.65	420	10.8	13.6	420
430	14.3	12.7	9.85	430	11.1	13.7	430
440	15.8	14.1	11.0	440	12.2	15.2	440
450	18.2	16.2	12.7	450	14.1	17.5	450
460	19.7	17.5	13.7	460	15.3	18.9	460
470	20.2	18.1	14.2	470	15.8	19.5	470
480	20.5	18.3	14.4	480	16.0	19.8	480
490	20.6	18.4	14.5	490	16.1	19.8	490
500	20.9	18.7	14.8	500	16.4	20.2	500
510	21.1	18.8	14.9	510	16.4	20.3	510
520	21.1	18.9	14.9	520	16.5	20.3	520
530	21.3	19.0	15.1	530	16.7	20.5	530
540	21.2	19.0	15.0	540	16.6	20.4	540
550	21.1	18.8	14.9	550	16.5	20.3	550
560	21.3	19.0	15.1	560	16.7	20.5	560
570	21.6	19.3	15.3	570	16.9	20.8	570
580	22.1	19.7	15.7	580	17.3	21.2	580
590	22.3	19.9	15.8	590	17.5	21.5	590
600	22.5	20.0	15.9	600	17.6	21.6	600
610	22.6	20.2	16.0	610	17.7	21.8	610
620	22.6	20.1	16.1	620	17.7	21.8	620
630	22.6	20.1	16.2	630	17.7	21.7	630
640	23.1	20.6	16.6	640	18.2	22.3	640
650	23.6	21.1	16.9	650	18.6	22.8	650
660	24.0	21.4	17.2	660	18.9	23.1	660
670	24.3	21.7	17.4	670	19.2	23.4	670
680	24.3	21.7	17.5	680	19.2	23.4	680
690	24.3	21.7	17.5	690	19.2	23.4	690
700	24.2	21.7	17.5	700	19.2	23.0	700
710	24.1	21.5	17.4	710	19.1	23.2	710
720	23.9	21.4	17.3	720	19.0	23.0	720
730	23.8	21.3	17.2	730	18.9	22.9	730
740	23.6	21.1	17.2	740	18.8	22.8	740
750	23.5	21.0	17.1	750	18.7	22.6	750
760	23.3	20.9	17.0	760	18.6	22.5	760
770	23.2	20.8	16.9	770	18.5	22.3	770
780	23.1	20.6	16.8	780	18.4	22.2	780
790	22.9	20.5	16.7	790	18.3	22.1	790
800	22.8	20.4	16.7	800	18.2	21.9	800

[a] J_λ values are in units of 10^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Table 6

J_λ VALUES AT 30°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.0000768	0.00000203	0.000000213	290	0.000000457	0.0000352	290
300	0.0831	0.0457	0.00835	300	0.0208	0.0704	300
310	1.14	0.787	0.300	310	0.480	1.02	310
320	2.84	2.13	1.06	320	1.47	2.60	320
330	5.02	3.88	2.13	330	2.81	4.62	330
340	5.49	4.30	2.48	340	3.19	5.08	
350	6.28	4.88	2.89	350	3.68	5.74	350
360	6.49	5.15	3.10	360	3.91	6.02	360
370	8.09	6.43	3.95	370	4.94	7.51	370
380	7.93	6.25	3.95	380	4.91	7.37	380
390	8.12	6.53	4.12	390	5.08	7.55	390
400	11.1	8.97	5.73	400	7.02	10.4	400
410	14.1	11.4	7.37	410	8.99	13.2	410
420	14.7	12.-	7.81	420	9.46	13.7	420
430	14.9	12.2	8.00	430	9.66	13.9	430
440	16.5	13.5	8.94	440	10.8	15.4	440
450	19.0	15.5	10.4	450	12.4	17.8	450
460	20.6	16.8	11.3	460	13.5	19.2	460
470	21.2	17.3	11.7	470	13.9	19.8	470
480	21.5	17.6	11.9	480	14.2	20.1	480
490	21.5	17.7	12.0	490	14.3	20.1	490
500	21.9	18.0	12.2	500	14.5	20.5	500
510	22.1	18.1	12.3	510	14.6	20.6	510
520	22.1	18.1	12.4	520	14.7	20.7	520
530	22.3	18.3	12.5	530	14.8	20.9	530
540	22.1	18.2	12.4	540	14.7	20.6	540
550	22.1	18.1	12.4	550	14.7	20.6	550
560	22.6	18.3	12.5	560	14.8	20.8	560
570	22.6	18.6	12.7	570	15.1	21.1	570
580	23.1	19.0	13.0	580	15.4	21.6	580
590	23.3	19.2	13.2	590	15.6	21.8	590
600	23.5	19.3	13.3	600	15.7	22.0	600
610	23.7	19.5	13.4	610	15.8	22.1	610
620	23.6	19.3	13.6	620	15.9	22.1	620
630	23.6	19.2	13.7	630	16.0	22.1	630
640	24.2	19.8	14.0	640	16.3	22.6	640
650	24.7	20.4	14.2	650	16.7	23.1	650
660	25.1	20.7	14.4	660	16.9	23.5	660
670	25.4	21.0	14.7	670	17.2	23.8	670
680	25.4	21.0	14.7	680	17.2	23.8	680
690	25.4	21.0	14.8	690	17.3	23.8	690
700	25.3	21.0	14.8	700	17.3	23.7	700
710	25.2	20.8	14.7	710	17.2	23.6	710
720	25.0	20.7	14.6	720	17.1	23.4	720
730	24.9	20.6	14.6	730	17.0	23.3	730
740	24.8	20.5	14.5	740	16.9	23.2	740
750	24.6	20.4	14.5	750	16.8	23.0	750
760	24.4	20.3	14.4	760	16.8	22.9	760
770	24.3	20.1	14.3	770	16.7	22.7	770
780	24.1	20.0	14.3	780	16.6	22.6	780
790	24.0	19.9	14.2	790	16.5	22.5	790
800	23.8	19.8	14.2	800	16.4	22.3	800

[a] J_λ values are in units of 10^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Table 7

J_λ VALUES AT 40°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.0000136	0.000000121	0.000000000615	290	0.0000000814	0.00000349	290
300	0.0769	0.0293	0.00145	300	0.00939	0.0587	300
310	1.12	0.618	0.132	310	0.298	0.940	310
320	2.87	1.81	0.591	320	1.04	2.49	320
330	5.11	3.41	1.31	330	2.90	4.49	330
340	5.62	3.83	1.58	340	2.43	4.77	340
350	6.35	4.39	1.88	350	2.84	5.64	350
360	6.61	4.65	2.05	360	3.05	5.93	360
370	8.32	5.86	2.64	370	3.88	7.43	370
380	8.17	5.80	2.67	380	3.88	7.30	380
390	8.37	5.99	2.82	390	4.05	7.50	390
400	11.5	8.26	3.97	400	5.64	10.3	400
410	14.6	10.5	5.15	410	7.26	13.1	410
420	15.2	11.1	5.51	420	7.69	13.9	420
430	15.5	11.3	6.69	430	7.89	15.4	430
440	17.1	12.5	6.41	440	8.82	17.8	440
450	19.7	14.5	7.47	450	10.2	19.2	450
460	21.3	15.7	8.15	460	11.1	19.8	460
470	22.0	16.2	8.51	470	11.5	20.1	470
480	22.3	16.5	8.74	480	11.8	20.2	480
490	22.3	16.6	8.83	490	11.9	20.6	490
500	22.7	16.9	8.99	500	12.1	20.7	500
510	22.9	17.0	9.07	510	12.2	20.8	510
520	22.9	17.0	9.14	520	12.3	21.0	520
530	23.2	17.2	9.24	530	12.4	21.0	530
540	23.0	17.1	9.18	540	12.3	20.8	540
550	22.9	17.0	9.15	550	12.3	20.7	550
560	23.1	17.2	9.23	560	12.4	20.9	560
570	23.5	17.4	9.38	570	12.6	21.2	570
580	24.0	17.8	9.62	580	12.9	21.9	580
590	24.2	18.0	9.79	590	13.1	21.9	590
600	24.4	18.2	9.85	600	13.2	22.1	600
610	24.6	18.3	9.93	610	13.2	22.2	610
620	24.5	18.3	10.2	620	13.4	22.2	620
630	24.5	18.3	10.2	630	13.5	22.1	630
640	25.1	18.8	10.5	640	13.8	22.7	640
650	25.7	19.2	10.7	650	14.1	23.3	650
660	26.1	19.5	10.9	660	14.3	23.6	660
670	26.4	19.8	11.1	670	14.5	24.0	670
680	26.3	19.9	11.1	680	14.6	24.0	680
690	26.4	19.9	11.2	690	14.6	24.0	690
700	26.4	19.9	11.3	700	14.7	24.0	700
710	26.2	19.8	11.2	710	14.6	23.9	710
720	26.1	19.7	11.2	720	14.6	23.7	720
730	25.9	19.6	11.2	730	14.5	23.5	730
740	25.8	19.5	11.2	740	14.5	23.4	740
750	25.6	19.4	11.2	750	14.4	23.3	750
760	25.5	19.3	11.2	760	14.4	23.1	760
770	25.3	19.2	11.3	770	14.3	23.0	770
780	25.2	19.1	11.3	780	14.3	22.4	780
790	25.0	19.0	11.2	790	14.2	22.7	790
800	24.8	1.89	11.2	800	14.1	22.6	800

[a] J_λ values are in units of 10^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10 nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Table 8

J_λ VALUES AT 50°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.00000185	0.000000200	0.0000000112	290	0.0000000391	0.00000152	290
300	0.0635	0.0140	0.0000681	300	0.00296	0.0433	300
310	1.05	0.423	0.321	310	0.147	0.810	310
320	2.81	1.41	0.214	320	0.610	2.28	320
330	5.10	2.78	0.555	330	1.33	4.23	330
340	5.64	3.19	0.711	340	1.59	4.73	340
350	6.41	3.70	0.864	350	1.88	5.40	350
360	6.75	3.96	0.953	360	2.04	5.71	360
370	8.46	5.03	1.23	370	2.63	7.18	370
380	8.32	5.01	1.28	380	2.66	7.09	380
390	8.56	5.21	1.37	390	2.80	7.31	390
400	11.8	7.22	1.95	400	3.93	10.1	400
410	15.0	9.27	2.57	410	5.09	12.8	410
420	15.7	9.79	2.79	420	5.45	13.5	420
430	15.9	10.0	2.92	430	5.62	13.7	430
440	17.6	11.2	3.33	440	6.33	15.2	440
450	20.3	12.9	3.92	450	7.37	17.6	450
460	22.0	14.0	4.31	460	8.05	19.0	460
470	22.7	14.5	4.56	470	8.40	19.7	470
480	23.1	14.8	4.70	480	8.62	20.0	480
490	23.1	15.0	4.78	490	8.72	20.1	490
500	23.5	15.2	4.88	500	8.87	20.4	500
510	23.7	15.3	4.94	510	9.00	20.6	510
520	23.8	15.4	4.98	520	9.03	20.6	520
530	24.0	15.6	5.05	530	9.12	20.8	530
540	23.8	15.5	5.02	540	9.07	20.7	540
550	23.7	15.4	5.01	550	9.05	20.6	550
560	24.0	15.5	5.04	560	9.11	20.8	560
570	24.3	15.8	5.11	570	9.26	21.1	570
580	24.8	16.1	5.27	580	9.50	21.6	580
590	25.1	16.4	5.38	590	9.66	21.8	590
600	25.3	16.5	5.42	600	9.73	22.0	600
610	25.5	16.6	5.47	610	9.80	22.1	610
620	25.4	16.8	5.61	620	9.96	22.1	620
630	25.3	17.0	5.77	630	10.1	22.1	630
640	26.0	17.3	5.93	640	10.4	22.7	640
650	26.7	17.6	6.10	650	10.6	23.3	650
660	27.1	17.8	6.24	660	10.8	23.6	660
670	27.5	18.1	6.39	670	11.0	24.0	670
680	27.5	18.2	6.47	680	11.0	24.0	680
690	27.5	18.2	6.56	690	11.1	24.0	690
700	27.5	18.2	6.64	700	11.2	24.0	700
710	27.3	18.1	6.67	710	11.2	29.9	710
720	27.2	18.1	6.72	720	11.2	23.8	720
730	27.0	18.0	6.75	730	11.2	23.6	730
740	26.9	17.9	6.78	740	11.2	23.5	740
750	26.7	17.8	6.82	750	11.1	23.4	750
760	26.6	17.8	6.82	760	11.1	23.3	760
770	26.4	17.7	6.82	770	11.1	23.1	770
780	26.3	17.6	6.82	780	11.1	23.0	780
790	2.61	17.5	6.80	790	11.0	22.9	790
800	26.0	17.4	6.80	800	11.0	22.8	800

[a] J_λ values are in units of 10^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10-nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Table 9

J_λ VALUES AT 60°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.00000155	0.00000000845	0.00000000136	290	0.00000000486	0.000000441	290
300	0.0466	0.00411	0.0000297	300	0.000556	0.0273	300
310	0.024	0.231	0.0000297	310	0.0544	0.643	310
320	2.67	0.937	0.0277	320	0.275	1.99	320
330	4.99	2.00	0.0878	330	0.656	3.83	330
340	5.60	2.38	0.140	340	0.818	4.36	340
350	6.41	2.80	0.175	350	0.921	5.02	350
360	6.79	3.03	0.190	360	1.07	5.35	360
370	8.35	3.90	0.246	370	1.39	6.77	370
380	8.45	3.82	0.249	380	1.42	6.72	380
390	8.72	4.12	0.264	390	1.50	6.97	390
400	17.0	5.77	0.375	400	2.12	9.64	400
410	15.4	7.46	0.491	410	2.77	12.3	410
420	16.1	7.95	0.530	420	2.99	13.0	420
430	16.4	8.19	0.553	430	3.10	13.3	430
440	18.3	9.19	0.630	440	3.52	14.8	440
450	21.1	10.7	0.740	450	4.11	17.1	450
460	22.8	11.6	0.813	460	4.51	18.6	460
470	23.6	12.1	0.857	470	4.72	19.2	470
480	24.0	12.4	0.885	480	4.87	19.6	480
490	24.1	12.5	0.899	490	4.94	19.7	490
500	24.5	12.8	0.909	500	5.03	20.0	500
510	24.7	12.9	0.915	510	5.08	20.2	510
520	24.8	13.0	0.918	520	5.12	20.3	520
530	25.0	13.1	0.917	530	5.18	20.5	530
540	24.9	13.0	0.904	540	5.14	20.3	540
550	24.8	13.0	0.896	550	5.13	20.3	550
560	25.0	13.1	0.890	560	5.16	20.5	560
570	25.4	13.3	0.889	570	5.23	20.8	570
580	25.9	13.6	0.918	580	5.38	21.2	580
590	26.2	13.8	0.943	590	5.49	21.5	590
600	26.4	13.9	0.953	600	5.53	21.7	600
610	26.6	14.0	0.961	610	5.57	21.8	610
620	26.6	14.2	1.01	620	5.69	21.9	620
630	26.5	14.4	1.05	630	5.83	22.0	630
640	27.3	14.7	1.11	640	6.00	22.6	640
650	28.0	15.0	1.17	650	6.14	23.1	650
660	28.5	15.3	1.22	660	6.28	23.1	660
670	28.9	15.5	1.27	670	6.42	23.8	670
680	28.9	15.6	1.30	680	6.48	23.8	680
690	29.0	15.7	1.34	690	6.56	23.9	690
700	29.0	14.7	1.42	700	6.64	23.9	700
710	28.9	15.7	1.47	710	6.67	23.8	710
720	28.7	15.6	1.53	720	6.71	23.7	720
730	28.6	15.6	1.58	730	6.75	23.6	730
740	28.5	15.6	1.64	740	6.78	23.5	740
750	28.3	15.5	1.69	750	6.82	23.4	750
760	28.2	15.5	1.70	760	6.81	23.3	760
770	28.0	15.4	1.71	770	6.81	23.2	770
780	27.9	15.4	1.72	780	6.81	23.1	780
790	27.7	15.3	1.73	790	6.79	23.0	790
800	27.6	15.3	1.75	800	6.79	22.9	800

[a] J_λ values are in units of 19^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10-nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Table 10

J_λ VALUES AT 70°N. LATITUDE

Wavelength Center[b]	Summer Solstice[a]	Equinox[a]	Winter Solstice[a]	Wavelength Center[b]	Fall or Winter Avg.[a]	Spring or Summer Avg.[a]	Wavelength Center[b]
290	0.000000223	0.000000145	0.00	290	0.00000000290	0.000000178	290
300	0.0280	0.0000459	0	300	0.0000247	0.0136	300
310	0.764	0.0822	0	310	0.0134	0.460	310
320	2.49	0.466	0	320	0.0869	1.64	320
330	4.92	1.13	0	330	0.230	3.34	330
340	5.66	1.42	0	340	0.299	3.91	340
350	6.57	1.71	0	350	0.364	4.57	350
360	7.02	1.88	0	360	0.400	4.91	360
370	8.91	2.45	0	370	0.521	6.27	370
380	8.87	2.50	0	380	0.532	6.27	380
380	9.22	2.66	0	390	0.568	6.56	390
400	12.8	3.77	0	400	0.807	9.13	400
410	16.4	4.94	0	410	1.059	11.8	410
420	17.4	5.33	0	420	1.147	12.5	420
430	17.8	5.54	0	430	1.20	12.8	430
440	19.8	6.30	0	440	1.36	14.4	440
450	23.0	7.37	0	450	1.60	15.7	450
460	24.9	8.09	0	460	1.76	18.1	460
470	25.8	8.48	0	470	1.85	18.8	470
480	26.4	8.75	0	480	1.91	19.2	480
490	26.6	8.89	0	490	1.95	19.4	490
500	27.0	9.05	0	500	1.98	19.7	500
510	27.2	9.15	0	510	2.00	19.9	510
520	27.4	9.23	0	520	2.02	20.0	520
530	27.6	9.34	0	530	2.04	20.2	530
540	27.4	9.29	0	540	2.03	20.1	540
550	27.3	9.27	0	550	2.02	20.0	550
560	27.6	9.33	0	560	2.03	20.2	560
570	28.0	9.47	0	570	2.05	20.5	570
580	28.6	9.74	0	580	2.11	21.0	580
590	29.0	9.93	0	590	2.16	21.3	590
600	29.2	10.0	0	600	2.18	21.5	600
610	29.4	10.1	0	610	2.20	21.6	610
620	29.8	10.3	0	620	2.26	21.9	620
630	30.1	10.5	0	630	2.33	22.2	630
640	30.8	10.8	0	640	2.40	22.7	640
650	31.3	11.1	0	650	2.48	23.1	650
660	31.9	11.1	0	660	2.54	23.5	660
670	32.4	11.5	0	670	2.61	23.9	670
680	32.5	11.6	0	680	2.64	24.0	680
690	32.7	11.8	0	690	2.69	24.1	690
700	32.8	11.9	0	700	2.74	24.2	700
710	32.7	11.9	0	710	2.77	24.1	710
720	32.6	12.0	0	720	2.81	24.1	720
730	32	12.0	0	730	2.84	24.0	730
740	3	12.0	0	740	7.87	24.0	740
750	3	12.1	0	750	2.91	23.9	750
760	32	12.0	0	760	2.91	23.8	760
770	32.5	12.0	0	770	2.92	23.8	770
780	32.0	12.0	0	780	2.92	23.7	780
790	31.8	12.0	0	790	2.92	23.6	790
800	31.7	12.0	0	800	2.92	23.5	800

[a] J_λ values are in units of 10^{19} photons cm^{-2} day^{-1}.

[b] Wavelength intervals are uniformly 10-nm wide, extending from 5 nm lower than the center wavelength to 5 nm higher. Thus, the first interval centered on 290 extends from 285-295 nm.

Appendix B. Operation of the Gas Handling System

The following procedure briefly describes the recommended typical and detailed operation of a gas handling system. [Adapted from the report by Pitts et al. (1981)].

(1) Close all stopcocks and turn on the rotary pump (A). Open stopcock 4 and place a Dewar containing liquid nitrogen around trap (D). Measure the pressure with the thermocouple gauge H_1. When the pressure is less than 0.1 torr (<0.013 kPa) open stopcocks 5 and 10, pump out this portion of the manifold, and measure the pressure with the thermocouple gauge H_2. When the pressure falls below 10^{-2} torr (<1.3 x 10^{-3} kPa), open stopcock 7 and evacuate F containing activated Linde Molecular Sieve 4A or an equivalent grade. Heat F to approximately 150 °C for 1-2 h under vacuum until the pressure falls to less than 10^{-2} torr (<1.3 x 10^{-3} kPa) as measured on thermocouple gauge H_2. Open stopcocks 6, 9, and 11 and pump until H_2 falls below 10^{-2} torr (<1.3 x 10^{-3} kPa).

(2) Turn on the diffusion pump (C) and when this pump has reached operating temperature, open stopcocks 2 and 3 and close stopcock 4. Pump on the manifold until the pressue is 10^{-5} torr (1.3 x 10^{-6} kPa) as measured by the ionization gauge (I) and zero on the capacitance manometer (G). It should be noted that the ionization gauge (I) should only be used when H_2 indicates a pressure less than 10^{-2} torr (<1.3 x 10^{-3} kPa).

(3) It is good practice, after the gas-phase spectrum has been obtained, to evacuate the gas absorption cell (K) and the trap (F) prior to shutting down the gas handling system. The gas

handling system can be shut down by the following procedure: (a) close stopcocks 5 to 11, (b) switch off the diffusion pump; (c) close stopcocks 2 and 3 and open 4, after the diffusion pump is cool; (d) remove the Dewar from trap (D) and allow it to warm up; (e) then close stopcock 4 and switch off the rotary pump; and (f) open stopcock 1 to admit air to the rotary pump, thus preventing "suck-back" of the rotary pump oil. With this procedure, the vacuum manifold, the trap D, and the diffusion pump are left under vacuum. The method of cleaning the liquid reservoir (J) is left to the discretion of the tester. However, as a final step it should be cleaned with reagent grade methanol or dichloromethane as solvent and dried. It is then ready for use. In operating a vacuum system with the diffusion pump working, do not expose the diffusion pump to pressures > 0.1 torr of air ($< 1.3 \times 10^{-2}$ kPa)to avoid the degradation of the pump oil.

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